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NON-AQUEOUS ELECTROLYTIC SOLUTION SECONDARY BATTERY  
[Hisui denkaieki niji denchi]

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## Claims

1. A non-aqueous electrolytic solution secondary battery comprised of: a cathode that is comprised of lithium<sub>1-x</sub> CoO<sub>2</sub> ( $0 \leq x < 1$ ) or is comprised of the same with a portion of the cobalt thereof replaced with a transition metal, to which zirconium (Zr) has been added; an anode comprised of lithium, a lithium alloy or a carbon substance; and a non-aqueous electrolytic solution.

2. The non-aqueous electrolytic solution secondary battery recorded in Claim 1, for which the molar ratio of the aforementioned zirconium added is 1-10% with respect to the aforementioned cobalt.

## Detailed explanation of the invention

[0001]

Technical field of the invention

The present invention pertains to a non-aqueous electrolytic solution secondary battery; it particularly pertains to an improvement in the characteristics of a battery for which a lithium compound oxide is used as the cathode.

[0002]

Prior art

In recent years there has been an increasing trend to make electronic devices such as AV devices or personal computers portable and cordless, and the demand has increased for compact, lightweight and high energy density secondary batteries for use as power sources to drive them. In this regard the expectations are high for non-aqueous secondary batteries – particularly lithium secondary batteries – which have a high voltage and high energy density.

[0003]

To meet this demand, compound oxides (hereinafter called 'lithium compound oxides') which have lithium and a transition metal as the main components – for example,  $\text{LiCoO}_2$ ,  $\text{LiNiO}_2$  (for example, U.S. Patent No. 4302518) or  $\text{LiCo}_x\text{Ni}_{1-x}\text{O}_2$  ( $x \leq 0.27$ ) (Japanese Kokai Patent Application No. Sho 62[1987]-264560) – which are laminated compounds that can perform intercalation and deintercalation on lithium, have been proposed as the cathodic active substance; and 4V high energy density secondary batteries which use these active substances are being developed.

[0004]

Problems to be solved by the invention

$\text{Li}_{1-x}\text{CoO}_2$  ( $0 \leq x < 1$ ) (hereinafter called ' $\text{LiCoO}_2$ ') exhibits a potential of 4V or greater with respect to lithium, and when used as the cathodic active substance a secondary battery having high energy density can be obtained. However, because the potential is high it adversely affects the battery's charge-discharge characteristics, for example by breaking down the propylene carbonate or dimethoxyethane which forms the organic electrolytic solution, thus degrading the battery's characteristics. In light of this problem it has been proposed that compound oxides for which a portion of the cobalt is replaced with nickel (Japanese Kokai Patent Application Sho 63[1988]-299056), iron (Japanese Kokai Patent Application Sho 63[1988]-211564), or aluminum, tin, indium (Japanese Kokai Patent Application Sho 62[1987]-90863) be used to modify the properties of the cathodic active substance and thus obtain excellent charge-discharge characteristics. However, compound oxides for which a portion of the cobalt is replaced with elements such as these tend to have a low discharge voltage, so the original high voltage and high energy density characteristics are reduced. Furthermore, when these types of lithium compound

oxides are stored at a high temperature while charged they have the same problem as with  $\text{LiCoO}_2$  in that their capacity is significantly reduced.

[0005]

The purpose of the present invention is to solve these problems by providing a secondary battery which maintains a high operating voltage, excellent charge-discharge and storage characteristics.

[0006]

Means to solve the problem

To solve these problems, the present invention has as its basis the discovery that, when zirconium<sup>1</sup> is added to the  $\text{LiCoO}_2$ , which is the cathodic active substance, a non-aqueous electrolytic solution secondary battery which generates a high voltage and which has excellent charge-discharge and storage characteristics can be obtained.

[0007]

Function

When a battery having  $\text{LiCoO}_2$  as the cathodic active substance is stored at a high temperature, the battery's capacity and cycle characteristics are severely degraded after storage. It is believed that this is due to decomposition of the electrolytic solution and damage to the crystalline structure. It is extremely critical that crystal damage and decomposition of the electrolytic solution with respect to this high-potential  $\text{LiCoO}_2$  be controlled in order to obtain a useful battery.

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<sup>1</sup> [Translator's Note: Paragraph 0006 has been amended to replace the word 'lanthanum' with 'zirconium' (as the additive); however, this change is not reflected in paragraph 0008 or in Table 1.]

[0008]

With the present invention, by adding lanthanum to the  $\text{LiCoO}_2$  the  $\text{LiCoO}_2$  particles are covered and thus stabilized by lanthanum oxide ( $\text{La}_2\text{O}_3$ ), a compound oxide of lithium and lanthanum ( $\text{LiLaO}_2$ ), or a compound oxide of lanthanum and cobalt ( $\text{LaCoO}_3$ ); consequently, decomposition of the electrolytic solution and damage to the crystalline structure do not occur even when there is a high potential, and a cathodic active substance with excellent cycle and storage characteristics is obtained. Furthermore, this effect cannot be obtained merely by mixing zirconium or a zirconium alloy with the  $\text{LiCoO}_2$ .

[0009]

#### Application example

In the following an application example of the present invention will be explained with reference to the figures.

[0010]

Zirconium oxide ( $\text{ZrO}_2$ ) was added to a mixture of  $\text{Li}_2\text{CO}_3$  and  $\text{CoCO}_3$  with a 1:1 atomic ratio of Li and Co, and this was baked in air at  $900^\circ\text{C}$  for 5 h to produce the cathodic active substance. The ratio of the added zirconium oxide ( $\text{ZrO}_2$ ) was expressed as mol% zirconium with respect to cobalt of the primary synthesized active material, the  $\text{LiCoO}_2$ , and the 6 varieties shown in Table 1 were investigated.

[0011]

TABLE 1

①	電 池	A	B	C	D	E	F
②	La 添加量 (モル%)	0	1	3	5	7	10

Key: 1 Battery  
2 Amount of La added (mol%)

[0012]

100 parts by weight of this synthesized cathodic active substance, 4 parts by weight of acetylene black, 4 parts by weight of graphite, and 7 parts by weight of a fluorine resin series adhesive were mixed as the cathode binder, and this was suspended in a carboxymethylcellulose solution to form a paste. This paste was applied to both surfaces of aluminum foil and after drying it was rolled to form a plate.

[0013]

For the anode 10 parts by weight of a fluorine resin series adhesive was mixed with 100 parts by weight of a carbon substance of baked coke and this was suspended in a carboxymethylcellulose solution to form a paste. This paste was applied to both surfaces of copper foil and after drying it was rolled to form a plate.

[0014]

Figure 1 shows a vertical cross section of a cylindrical battery used with the present application example. The battery was constructed by attaching leads respectively to the cathode and anode, winding these into a coil with a polypropylene separator interposed, and housing this in a battery case. The electrolytic solution used was a solution of equal amounts of propylene and ethylene carbonate in which lithium perchlorate was dissolved at a ratio of 1 mol/L, and this was sealed for use as a trial battery.

[0015]

In Figure 1, 1 is a battery case manufactured from a stainless steel resistant to organic electrolytic solution, 2 is a sealing plate provided with a safety valve, and 3 is insulation packing. 4 is the plate group, with the cathode and the anode wound into a coil with a separator interposed, and housed within the case. In addition, a cathode lead 5 extends from the aforementioned cathode and is connected to sealing plate 2, while an anode lead 6 extends from the anode and is connected to the bottom of battery case 1. In addition, 7 is an insulation ring, provided respectively at the top and bottom of plate group 4.

[0016]

A constant current charge-discharge test was performed with these trial batteries with the following conditions: charge-discharge current of 100 mAh, charge termination voltage of 4.1V, and discharge termination voltage of 3.0V. In addition, charging was repeated for 10 cycles, after which a storage test (hereinafter called 'high-temperature charged storage') was performed for 20 days at 60°C while they were in the charged state and the percent retained capacity was obtained for the batteries after storage.

[0017]

Figure 2 shows the relationship between the number of charge-discharge cycles and the discharge amount for batteries A-F. In addition, Figure 3 shows the relationship between the amount of zirconium added to the  $\text{LiCoO}_2$  and the percent retained capacity (capacity before storage/capacity after storage) for the corresponding batteries A-F after high-temperature charged storage F.



[0018]

From Figure 2, battery A to which no zirconium was added has a large initial discharge capacity; however, the capacity significantly decreases as the number of charge-discharge cycles increases, reaching 50% of the initial amount at 300 cycles. On the other hand, for batteries B-F to which zirconium was added, the capacity decreases as the amount added increases; however, the decrease in capacity as the number of charge-discharge cycles increases is significantly reduced compared to A, and batteries D-F to which 5 mol% or more of zirconium was added retained 80% or more of their initial capacity at 300 cycles.

[0019]

Furthermore, Figure 3 shows that by adding zirconium the percent of retained capacity for the batteries after high-temperature storage was greatly improved; whereas it was 52% for battery A to which no zirconium was added, it was more than 88% for battery D to which 5% was added. Furthermore, when the amount of zirconium added was increased there was little change in the percent retained capacity. For battery F, to which 10% zirconium was added, both the cycle and storage characteristics were excellent, but the percent of surface damage for the  $\text{LiCoO}_2$  was large, so the discharge capacity was relatively small. Therefore, it is appropriate for the amount of zirconium added to be approximately 5%.

[0020]

When a portion of the cobalt of the  $\text{LiCoO}_2$  is replaced with nickel (Japanese Kokai Patent Application Sho 63[1988]-299056), iron (Japanese Kokai Patent Application Sho 63[1988]-211564), or aluminum, tin, indium (Japanese Kokai Patent Application Sho 62[1987]-90863), it forms a solid

solution with the cobalt and becomes a compound oxide represented by  $\text{LiM}_y\text{Co}_{1-y}\text{O}_2$  (where  $0 \leq y \leq 1$  and M is Ni, Fe, Al etc.), so the surface stabilization effect is not obtained as it is with zirconium.

[0021]

Furthermore, these compound oxides for which a portion of the cobalt is replaced with a transition metal have a disadvantage in that the average voltage is low; however, when zirconium was added this voltage decrease was not observed. Accordingly, it can be said that zirconium is the optimal additive.

[0022]

In addition, with the present application example  $\text{Li}_2\text{CO}_3$  and  $\text{CoCO}_3$  were used as the starting materials when the cathode was synthesized; however, oxides, hydroxides and acetates of lithium and cobalt respectively can be used as well. Furthermore, the zirconium that was added was zirconium oxide, but other zirconium compounds can be used. Furthermore,  $\text{LiCoO}_2$  was used as the cathodic active substance, but the same effect was confirmed for compounds for which a portion of the cobalt therein was replaced with a transition metal. Furthermore, a carbon substance was used as the anode, but this also can be a lithium metal or alloy. Furthermore, a solution of equal amounts of propylene and ethylene carbonate in which lithium perchlorate was dissolved at a ratio of 1 mol/L was used as the electrolytic solution; however, it is the same with an electrolytic solution in which a lithium salt is dissolved.

[0023]

#### Effect of the invention

As is clear from the explanation above, by means of the present invention, by adding an appropriate amount of zirconium to the  $\text{LiCoO}_2$  which is the cathodic active substance, a non-aqueous electrolytic solution secondary battery with excellent charge-discharge cycle and high-temperature storage characteristics can be obtained.

#### Brief description of the figures

Figure 1 is a vertical cross section of a cylindrical battery according to an application example of the present invention.

Figure 2 is a graph of the charge-discharge cycle characteristics for said battery at 20°C.

Figure 3 is a graph of the relationship between the amounts of added zirconium and the percent retained capacity of the corresponding batteries after high-temperature storage.

#### Explanation of symbols

- 1 Battery case
- 2 Sealing plate
- 3 Insulation packing
- 4 Plate group
- 5 Cathode lead
- 6 Anode lead
- 7 Insulation ring

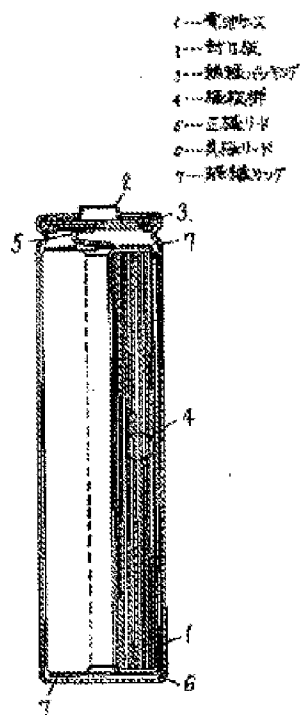


Figure 1

- Legend:
- 1 Battery case
  - 2 Sealing plate
  - 3 Insulation packing
  - 4 Plate group
  - 5 Cathode lead
  - 6 Anode lead
  - 7 Insulation ring

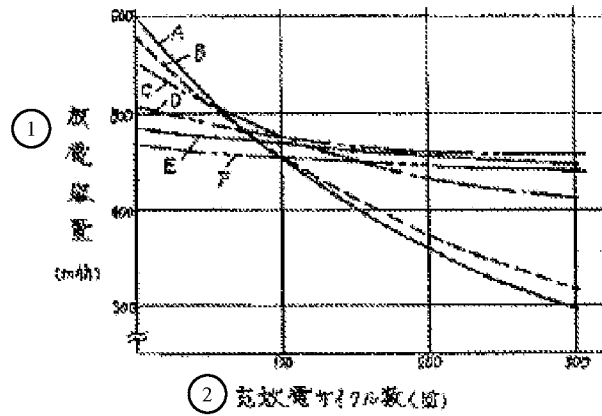


Figure 2

- Key: 1 Discharge amount (mAh)
- 2 Number of charge-discharge cycles (number of times)

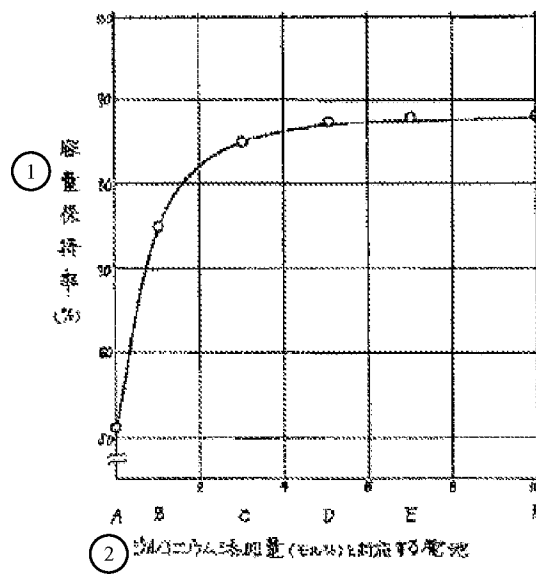


Figure 3

- Key: 1 Percent retained capacity (%)
- 2 Battery corresponding to the amount of zirconium added (mol%)